

Results of Phase I Groundwater Quality Assessment for Single-Shell Tank Waste Management Areas T and TX-TY at the Hanford Site

F. N. Hodges

February 1998

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Pacific Northwest National Laboratory (PNNL) conducted a Phase I, Resource Conservation and Recovery Act of 1976 (RCRA) groundwater quality assessment for the Richland Field Office of the U.S. Department of Energy (DOE-RL) under the requirements of the Federal Facility Compliance Agreement. The purpose of the investigation was to determine if the Single-Shell Tank Waste Management Areas (WMAs) T and TX-TY have impacted groundwater quality.

Waste Management Areas T and TX-TY, located in the northern part of the 200 West Area of the Hanford Site, contain the 241-T, 241-TX, and 241-TY tank farms and ancillary waste systems. These two units are regulated under RCRA interim-status regulations (under 40 CFR 265.93) and were placed in assessment groundwater monitoring because of elevated specific conductance in downgradient wells. Anomalous concentrations of technetium-99, chromium, nitrate, iodine-129, and cobalt-60 also were observed in some downgradient wells. Phase I assessment, allowed under 40 CFR 265, provides the owner-operator of a facility with the opportunity to show that the observed contamination has a source other than the regulated unit.

For this Phase I assessment, PNNL evaluated available information on groundwater chemistry and past waste management practices in the vicinity of WMAs T and TX-TY. Background contaminant concentrations in the vicinity of WMAs T and TX-TY are the result of several overlapping contaminant plumes resulting from past-practice waste disposal operations. This background has been used as baseline for determining potential WMA impacts on groundwater.

Examination of contaminant patterns in downgradient wells at the two WMAs indicate that:

- Elevated values of specific conductance in downgradient wells 299-W10-15 (WMA T) and 299-W10-17 (WMA TX-TY) are a result of elevated concentrations of sodium and nitrate originating outside of the WMAs.
- Elevated technetium-99 and co-contaminants (e.g., chromium, tritium, and nitrate) observed in well 299-W11-27, immediately downgradient to WMA T, are the result of a contaminant source within the WMA. Contaminant chemistry is consistent with a small volume tank waste source and limited lateral spreading indicates a source near the well.
- Elevated technetium-99 and co-contaminants (e.g., chromium, tritium, nitrate, iodine-129, and cobalt-60) in well 299-W14-12 at WMA TX-TY is consistent with a source within the WMA. Contaminant chemistry is consistent with a small volume tank waste source. An upgradient source is possible; however, without direct upgradient evidence for this alternative source the WMA must be assumed, for the purposes of this assessment, to be the source of the observed contamination.

Contents

Summary	iii
1.0 Introduction	1.1
1.1 Objectives	1.1
1.2 Scope	1.1
1.3 Report Contents	1.2
2.0 Specific Conductance	2.1
2.1 WMA T	2.1
2.2 WMA TX-TY	2.1
3.0 Phase I Assessment Findings	3.1
3.1 Groundwater Flow	3.1
3.2 Contaminant Concentration Patterns	3.5
3.2.1 Regional Patterns	3.5
3.2.2 Compositional Relationships	3.7
3.2.3 Key Assessment Wells	3.11
3.2.4 Compositional Relationships	3.27
3.3 Depth Variability	3.35
3.4 Evidence of Driving Forces	3.37
4.0 Conceptual Model	4.1
4.1 WMA T	4.1
4.1.1 Well 299-W10-15	4.1
4.1.2 Well 299-W11-27	4.1
4.2 WMA TX-TY	4.2
4.2.1 Well 299-W10-17	4.3
4.2.2 Well 299-W14-12	4.3
5.0 Conclusions	5.1

5.1 Recommendations	5.1
5.1.1 Compliance Issues	5.1
5.1.2 Near-Term Corrective Measures	5.1
5.1.3 Phase II Assessment Objectives	5.2
6.0 References	6.1
Appendix A - Summary of RCRA Monitoring Data	A.1

Figures

1.1	Locations of WMA T and WMA TX-TY in the 200 West Area	1.2
2.1	WMA T and WMA TX-TY Monitoring Network and Adjacent Facilities and Wells	2.2
2.2	Specific Conductance Values at WMA T as Function of Sample Date	2.3
2.3	Specific Conductance Values at WMA TX-TY as Function of Sample Date	2.3
3.1	Average Carbon Tetrachloride Concentrations in the 200 West Area During 1995	3.2
3.2	Water Table Map for the Vicinity of WMAs T and TX-TY Based on June 1997 Water Level Data	3.3
3.3	Hydrographs for Monitoring Wells at WMA T and WMA T-TY	3.4
3.4	Contaminant Plume Map for the Northern Portion of the 200 West Area	3.6
3.5	Contour Map of Groundwater Sodium/Calcium Values in the Vicinity of WMA T and WMA TX-TY	3.9
3.6	Contour Map of Groundwater Specific Conductance in the Vicinity of WMA T and WMA TX-TY	3.10
3.7	Map of Tritium/Technetium-99 in Vicinity of WMAs T and TX-TY	3.12
3.8	Waste Management Area T in the 200 West Area and Contaminant Concentrations/Activities in Wells 299-W10-15 and 299-W10-16	3.15
3.9	Waste Management Area T in the 200 West Area and Contaminant Concentrations/Activities in Wells 299-W11-27 and 299-W10-16	3.19
3.10	Waste Management Area TX-TY in the 200 West Area and Contaminant Concentrations/Activities in Wells 299-W10-17 and 299-W15-22	3.23
3.11	Waste Management Area TX-TY in the 200 West Area and Contaminant Concentrations/Activities in Wells 299-W14-12 and 299-W15-22	3.25
3.12	Plots of Technetium-99 versus Tritium, Nitrate, Iodine-129, and Cobalt-60 in Well 299-W14-12	3.28
3.13	Plots of Specific Conductance, Technetium-99, and Water Table Elevation as Function of Sample or Measurement Date in Well 299-W14-12	3.29

3.14	Calcium versus Sodium for Monitoring Wells at WMA T	3.30
3.15	Sodium/Calcium versus Calcium for Monitoring Wells at WMA T	3.30
3.16	Calcium versus Sodium for Monitoring Wells at WMA TX-TY	3.32
3.17	Sodium/Calcium versus Calcium for Monitoring Wells at WMA TX-TY	3.32
3.18	Plot of Tritium/Technetium-99 versus Technetium-99 for Wells at WMA T	3.34
3.19	Plot of Tritium/Technetium-99 versus Technetium-99 for Wells at WMA TX-TY	3.34
3.20	Plot of Nitrate/Technetium-99 versus Technetium-99 for Wells at WMA T	3.36
3.21	Plot of Nitrate/Technetium-99 versus Technetium-99 for Wells at WMA TX-TY	3.36
3.22	Schematic Illustration of Decrease in Observed Contaminant Concentrations as a Stratified Aquifer Drops Past the Pump Inlet	3.37
3.23	Photos Showing Flooding of the T Tank Farm after a Rapid Snow Melt Event in February 1979	3.38

Tables

3.1	Average Milliequivalents in Groundwater in Trigger Wells	3.13
3.2	Vertical Sampling Results from Well 299-W11-27	3.21

1.0 Introduction

This report presents the results and findings of a Phase I, *Resource Conservation and Recovery Act of 1976* (RCRA) groundwater quality assessment of Single-Shell Tank Waste Management Areas (WMAs) T and TX-TY as required by 40 CFR 265.93. Pacific Northwest National Laboratory^(a) conducted the assessment.

WMAs T and TX-TY, which contain the T and TX-TY Tank Farms, are located in the northern portion of the 200 West Area on the Hanford Site in Washington State (Figure 1.1). RCRA groundwater monitoring was initiated in 1989 and a RCRA monitoring network, meeting the minimum RCRA requirement of one upgradient and three downgradient wells at each WMA, was completed in 1992.

1.1 Objectives

Under 40 CFR 265, Subpart F, an owner or operator upon entering assessment monitoring must, as a minimum, determine the rate of transport and the extent and concentrations of hazardous waste or hazardous waste constituents in the groundwater. Under this regulation, however, the owner or operator may, upon entering assessment, attempt to make a determination that his site is not contaminating groundwater. In this context, Phase I of assessment monitoring is meant to indicate the early attempt to find other sources of the observed contamination.

The objective of the Phase I assessment is to determine whether the available evidence indicates an alternative source for the contamination. In the absence of definite evidence for an alternative source, it must be assumed that the WMA in question is the source. In this latter case, assessment monitoring must proceed with identification of sources and determination of the rate and extent of contaminant migration.

1.2 Scope

The scope of this report is limited to the consideration of information related to the source or sources of observed contamination. More detailed information on site geology and hydrology and the history of the WMAs is provided in Jensen et al. (1989), Caggiano and Goodwin (1991), Caggiano and Chou (1993), and numerous other documents (e.g., Graham et al. 1981; Connelly et al. 1992; Delaney et al. 1991; DOE/RL 1993; Lindsay 1995; Lindsay et al. 1991; and Tallman et al. 1979). These are included here for reference only.

(a) Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

-

-

Figure 1.1. Locations of WMA T and WMA TX-TY in the 200 West Area

1.3 Report Contents

Section 2.0 of this report provides some background on the specific conductance in downgradient wells at WMA T and TX-TY. Section 3.0 presents Phase I assessment findings. Section 4.0 describes a conceptual model developed to explain contaminants observed in downgradient wells at WMAs T and TX-TY. Conclusions are provided in Section 5.0.

2.0 Specific Conductance

This section briefly describes the monitoring network design and discusses specific conductance for WMAs T and TX-TY. Details describing WMAs T and TX-TY groundwater monitoring programs are provided by Jensen et al. (1989) and Caggiano and Goodwin (1991). Figure 2.1 shows details of the groundwater monitoring networks.

RCRA groundwater monitoring at WMAs T and TX-TY (T and TX-TY Tank Farms) moved from interim status detection level monitoring to assessment monitoring (40 CFR 265.93) in 1993 because of exceedances in specific conductance in downgradient wells at the two WMAs as set forth in the Phase I Assessment Plan (Caggiano and Chou 1993). Specific conductance is a RCRA indicator parameter that measures the quantity of ionic species in solution. An increase in specific conductance may indicate contamination, but is not in itself proof that contamination exists.

2.1 WMA T

Specific conductance in downgradient well 299-W10-15 at WMA T exceeded the critical mean of 1175 $\mu\text{Siemens/cm}$ established from four quarters of upgradient well (299-W10-16) data. Subsequently, the specific conductance has remained high (Figure 2.2), but has been below the critical mean since 1994. High values for specific conductance in well 299-W10-15 principally are a result of elevated sodium and nitrate.

A rapid increase in specific conductance in downgradient well 299-W11-27, starting in late 1995, has pushed the specific conductance in this well above the critical mean for WMA T (Figure 2.2). The increased specific conductance in this well is a result of increased concentrations of calcium, magnesium, nitrate, and sulfate. Increasing activities of technetium-99 and tritium are associated with the increasing specific conductance. Cobalt-60 is also present; however, iodine-129 does not appear to be a co-contaminant.

2.2 WMA TX-TY

WMA TX-TY was triggered into assessment monitoring because specific conductance in downgradient wells 299-W10-17 and 299-W14-12 exceeded the critical mean of 668 $\mu\text{S/cm}$ established from four quarters of upgradient well (299-W15-22) data. Subsequently, specific conductance values in well 299-W10-17 have shown some variability, but have remained well above the critical mean (Figure 2.3). High specific conductance values in well 299-W10-17 principally are a result of elevated concentrations of sodium and nitrate.

Specific conductance values in well 299-W14-12 dropped significantly between 1993 and mid-1996, but have stabilized at values above the critical mean during late 1996 and 1997 (Figure 2.3). Higher specific conductance values in well 299-W14-12 are associated with higher calcium, magnesium, nitrate, and sulfate, a pattern similar to that observed for well 299-W11-27 at WMA T. The higher values of specific conductance are associated with higher activities for technetium-99, tritium, iodine-129, and

cobalt-60.

-

-

Figure 2.1. WMA T and WMA TX-TY Monitoring Network and Adjacent Facilities and Wells

-

-

Figure 2.2. Specific Conductance Values at WMA T as Function of Sample Date.
Well 299-W10-16 is the upgradient well.

-

-

Figure 2.3. Specific Conductance Values at WMA TX-TY as Function of Sample Date.
Well 299-W15-22 is the upgradient well.

3.0 Phase I Assessment Findings

Phase I assessments require identifying chemical constituents that impact groundwater below the WMAs. This section describes groundwater flow directions in the vicinity of WMAs T and TX-TY, large-scale contaminant patterns (plumes) that may affect groundwater monitoring at the WMAs, and the contaminant chemistry in the downgradient monitoring wells that triggered these two sites into assessment. A summary of RCRA groundwater monitoring data for WMAs T and TX-TY is presented in Appendix A.

3.1 Groundwater Flow

Groundwater flow directions in the vicinity of WMAs T and TX-TY historically have been variable because of the influence of numerous effluent discharge sites in the 200 West Area. Before Hanford operations, groundwater flowed dominantly toward the east or northeast, driven by recharge in the Cold Creek Valley and topographically high areas along the western border of the Pasco Basin. During the late 1940s and 1950s, groundwater flow in the vicinity was controlled by discharge to T-Pond, located northwest of WMA T. Mounding beneath T-Pond resulted in south or southeastward groundwater flow beneath WMAs T and TX-TY, as indicated by available water level data for the 1950s. Separations operations at T-Plant ended in 1956 (Anderson 1990), and with decreased input to T-Pond, other groundwater recharge sources (U-pond, Z-cribs) became more important, and the flow direction changed to the north or northeast. Even after the closure of T-Pond; however, water was disposed to the T-4-2 Ditch south of T-Pond, and there may have been a small groundwater mound maintained in that area. Several plumes in the vicinity of WMA T exhibit a pattern consisting of two lobes separated by the area around the T-4-2 Ditch, indicating either dilution and/or diversion around this area. This is very evident in the specific conductivity map presented in Johnson (1993) and the 1995 plume map for carbon tetrachloride (Figure 3.1). The carbon tetrachloride map is particularly significant because the source of this contaminant is the Z-cribs (e.g., 216-Z-9, Figure 3.2) associated with the Plutonium Finishing Plant (PFP), approximately 1 km (0.6 mi) south of WMA T; therefore, the two-lobed pattern cannot be a result of two separate sources in the vicinity of WMA T. Current groundwater flow directions in the vicinity of WMAs T and TX-TY generally are toward the northeast, as indicated by Figure 3.2, a water table map based on June 1997 data.

Water table elevations across the 200 West Area have been declining since the decommissioning of U-Pond in 1985, a trend that has become much more pronounced since the cessation of effluent discharge throughout the 200 Areas in 1995. Hydrographs for monitoring wells at WMA T and WMA TX-TY (Figure 3.3) illustrate both the change in decline rate that started in 1995 and the decrease in hydraulic gradient across the area during the same time period. The decrease in gradient is especially evident in the hydrographs for wells at WMA TX-TY. Because of the increase in water table decline rate in 1995, groundwater monitoring wells at WMAs T and TX-TY will go dry much sooner than expected. In fact, all wells at the two WMAs probably will be dry by the end of 1998 and, as a case in point, water levels in well 299-W10-15 have dropped sufficiently so that the well could not be sampled in August 1997.

Figure 3.1. Average Carbon Tetrachloride Concentrations in the 200 West Area During 1995
(Dresel et al. 1996)

-

-

Figure 3.2. Water Table Map for the Vicinity of WMAs T and TX-TY Based on June 1997 Water Level Data

-

-

Figure 3.3. Hydrographs for Monitoring Wells at WMA T (a) and WMA TX-TY (b)

The unconfined aquifer beneath WMAs T and TX-TY is within Unit E of the Ringold Formation (Lindsay 1995). Gravels within Unit E of the Ringold have highly variable degrees of cementation, and thus, of hydraulic properties. In the vicinity of WMAs T and TX-TY, reported hydraulic conductivities range from 15 to 33 m/d (50 to 100 ft/d) and transmissivities from <47 to >93 m²/d (<500 to >1000 ft²/d) (Connelly et al. 1992; DOE/RL 1993). A fluorescein dye tracer test, carried out near the northwest corner of WMA T in 1974 as part of the T-106 tank leak study, indicated groundwater flow velocities on the order of 0.4 m/d (1.3 ft/d) (Routson et al. 1979). On the basis of the water table map presented by Routson et al. (1979), the hydraulic gradient presently is approximately half of the value it was in 1974 when the test was performed. Therefore on the basis of test results, a best estimate for current groundwater flow velocity is 0.2 m/d (0.7 ft/d).

3.2 Contaminant Concentration Patterns

Contaminant concentration patterns, both spatial and temporal, are important in understanding the nature and possible origins of contaminants detected in groundwater. In assessment monitoring it is important to understand the nature and distribution of both the contaminants detected in the wells of the site in question and of any outside sources of contamination that may be affecting the site. This section examines 1) contaminant patterns originating outside of the tank farms, and 2) the chemistry of groundwater in the trigger wells, to try to establish whether these outside contaminant sources are responsible for contaminants observed in the trigger wells. In this examination extensive use is made of ratios between mobile (high-solubility, little or no sorption) waste constituents such as nitrate, tritium, and technetium-99. This is a standard geochemical technique for dealing with mixing problems and helps to delineate the influences of the multiple waste management activities that have impacted groundwater quality in the area around WMA T and WMA TX-TY.

3.2.1 Regional Patterns

Groundwater in the area around WMAs T and TX-TY contains multiple, overlapping contaminant plumes, including nitrate, tritium, and carbon tetrachloride. These plumes result principally from waste management operations related to T-Plant; other 200 West operations, principally those associated with the PFP (234-5); and potentially, from the T and TX-TY Tank Farms. The extent of these plumes are indicated in various reports (Johnson 1993; Dresel et al. 1996; Dresel et al. 1997) and are illustrated in Figure 3.4. The major problems addressed in the following paragraphs is that of separating contamination resulting from these older waste disposal practices from contaminants that currently may be reaching groundwater from the tank farms or other adjacent sources.

In the immediate vicinity of WMAs T and TX-TY, the major known sources of groundwater contamination are the complex of cribs and trenches (T-7, T-5, and T-32) and T-7F tile field immediately west of WMA-T and the crib and tile field (T-19) immediately south of WMA-TX-TY (Figure 2.1). Based on data summarized in DOE/RL (1992) the T-7 crib and tile field received 110 million liters of tank supernate between 1948 and 1955, while the adjacent T-5 trench and T-32 crib received 2.6 million liters and 29 million liters, respectively, during the same period. The T-19 crib and tile field, used between 1951 and 1980, received approximately 455 million liters of waste, mostly condensate from the 242-T evaporator. In addition, numerous cribs and ditches in the vicinity received lesser quantities of tank supernate, condensate,

and miscellaneous waste. The most significant of these is the T-25 Trench, a specific retention trench located on the west side of WMA TX-TY, that received 11 million liters of evaporator bottoms containing an estimated 218 Ci of technetium-99.

-

-

Figure 3.4. Contaminant Plume Map for the Northern Portion of the 200 West Area
(after Dresel et al. 1997)

Groundwater flow directions at WMA T and WMA TX-TY have changed with changing waste management practices in the 200 West Area. During the time of most active waste disposal in the vicinity of WMAs T and TX-TY (late 1940s and 1950s), groundwater flowed toward the south or southeast because of T Pond, and any contaminant plumes that developed would have moved in those directions. This scenario is supported by the fact that groundwater monitoring, during the mid to late 1950s, in well 299-W10-1, located immediately north of the T-5 Trench, shows little evidence of groundwater contamination, while analyses of groundwater from well 299-W10-2, located to the south (Figure 2.1), indicated gross beta activities as high as 1 to 2 million picocuries per liter. It is entirely possible that contaminants from the disposal facilities west of WMA T could have been pushed south as far as the PFP before being carried back to their current positions along with whatever waste was picked up along the way. Eight years (1948-1956) of groundwater flow, at 0.4 m/d (based on tracer test), would result in a travel distance of approximately 1.3 km; therefore, there would have been adequate travel time for the main mass of the plume to reach the vicinity of PFP, which is approximately 1 km to the south-southeast of T-7. Likewise, tritium-rich water emanating from T-19 could have been pushed a considerable distance southeastward before returning northward. The wide distribution of carbon tetrachloride in the northern portion of the 200 West Area is mute testimony to the influence of disposal at PFP. The relatively small quantities of carbon tetrachloride (880 L) sent to the T-19 Crib and Tile Field between 1973 and 1976 (Rohay 1994) is insignificant compared the estimated 470,000 L disposed of at PFP. The complexity of contaminant patterns in this part of the 200 West Area is a result of this back-and-forth groundwater movement and mixing of contaminants from various sources.

The complexity of contaminants and potential impact of waste disposal at PFP in this area is illustrated by deeper samples taken from well 299-W10-1, located immediately west of WMA T, between 1990 and 1996. Groundwater chemistry in these samples is completely different from any of the surrounding wells, having high sodium (>100,000 ppb), high calcium (>200,000 ppb), high nitrate (>1,000,000 ppb), and high carbon tetrachloride (>2,000 ppb). This chemistry is what would be expected to result from the disposal of large quantities of concentrated nitric acid and carbon tetrachloride to cribs in the vicinity of PFP (i.e., 216-Z-1A) (Price et al. 1979). The high calcium concentration would be the result of dissolution of vadose zone calcium carbonate by nitric acid during transport. Water from this source could offer a strong nitrate component without tritium or technetium-99 as co-contaminants.

3.2.2 Compositional Relationships

Ratios between various groundwater constituents are important because they often, despite dilutions or other insults, retain information about origins and/or processes. In the following paragraphs constituent ratios are discussed as a means to gain insight into the origin and distributions of various groundwater plumes in the vicinity of WMAs T and TX-TY. Given the wide range of variation in groundwater chemistry in the vicinity of these two WMAs, it is not reasonable to expect one upgradient monitoring well to truly represent the range of upgradient effects on downgradient wells. Thus, an understanding of the nature of various contamination plumes present in the area is vital to understanding groundwater chemistry observed in downgradient wells.

3.2.2.1 Sodium/Calcium Ratio

The ratio of sodium to calcium in groundwater is important because of the way that tank waste interacts with minerals as it passes through the vadose zone. Tank waste, whether in the tanks or supernate

cascaded to various cribs and trenches, is principally a concentrated nitric acid solution that has been over neutralized with sodium hydroxide, leaving a liquid fraction that is a highly concentrated (multimolar) sodium nitrate solution, often referred to as “high salt” waste. When tank waste contacts the vadose zone, the process is essentially the same as backflushing a water softener with a concentrated sodium chloride brine. The high sodium concentrations in the liquid results in the replacement of exchangeable cations with sodium, with the exchangeable cations, principally calcium and magnesium, going into solution.

When large volumes of high-sodium waste are disposed to ground, for instance, the disposal of approximately 200 million liters of tank supernate to the cribs and tile field immediately west of the T Tank Farm, the ion exchange capacity of the underlying vadose is greatly exceeded, and the effects of ion exchange are swamped by the large quantity of sodium, resulting in high values for sodium/calcium in water reaching the water table. In the case of a relatively small volume leak or spill, however, the ion exchange process significantly affects the chemistry of any liquid reaching groundwater, resulting in lower sodium and higher calcium and magnesium concentrations in groundwater. Thus, sodium/calcium offers a tool for distinguishing the groundwater impacts of tank leaks or spills from the impacts of cribs, ditches, and tile fields (Johnson 1997). Unfortunately, the distinction between large and small volume sources is qualitative because of uncertainty in the ionic exchange capacity of the deeper portions of the vadose and uncertainty in the volume of vadose contacted by the waste.

The values for sodium/calcium, in areas not directly affected by contaminants, are generally below 1.0 and most fall into a range between 0.2 and 0.7. The natural Hanford groundwater background value for sodium/calcium is near 0.4 (Johnson 1993), and Columbia River water has a sodium/calcium value near 0.7. Process water, consisting primarily of Columbia River water, has been disposed of in great quantities for over 50 years in various ponds, cribs, and ditches and has had a strong effect on groundwater chemistry in the 200 West Area. Most groundwater sodium/calcium values in the 200 West area, however, are well below those of Columbia River water, indicating that mixing and/or reaction with vadose and aquifer materials have resulted in a significant lowering of the ratio throughout the area.

In the area of WMAs T and TX-TY, there is an extensive plume^(a) of high sodium/calcium groundwater that covers a large area west of the WMAs and extends eastward across WMA T and the northern portion of WMA TX-TY (Figure 3.5). This is an area of high specific conductance (Figure 3.6), principally because of high concentrations of sodium and nitrate. The groundwater plume indicated by the two maps is almost certainly a result of large volume disposal of tank waste to the ground, and may be the remnant of past waste disposal activities along the western side of the two WMAs, as indicated above. Continued drainage from large volume waste disposal sites (e.g., T-7) along the western margin of WMA T cannot be ruled out; however, low technetium-99 activities in this area indicate that it is a minor source at best.

(a) In this paper, “plume” will be used to designate any volume of groundwater distinguishable by a specific component or ratio of components.

-

-

Figure 3.5. Contour Map of Groundwater Sodium/Calcium Values in the Vicinity of WMA T and WMA TX-TY

-

-

Figure 3.6. Contour Map of Groundwater-Specific Conductance in the Vicinity of WMA T and WMA TX-TY

3.2.2.2 Tritium/Techneium-99 Ratio

Tritium and technetium-99 are both present in tank waste liquids; however, various tank processes and/or operations can result in fractionation and higher tritium/technetium-99 ratio values. The principal causes of fractionation are processes that involve evaporation and condensation. Examples of this are the self-boiling tanks in WMA-S and SX and the operation of various evaporators, such as the 242-T Evaporator at the TX Tank Farm, to reduce tank waste volume. A second, less likely, mechanism is the existence of reducing conditions that would result in precipitation of technetium as a solid phase.

Within the vicinity of WMAs T and TX-TY, the principal mechanism for tritium-technetium-99 fractionation is operation of the 242-T Evaporator that sent approximately 455 million liters of condensate to the T-19 Crib and Tile Field between 1951 and 1980. Effluents discharged to T-19 had a very high tritium/technetium ratio. No data exist from the operational period; however, Colby and Petersen (1995), on the basis of operational data from the 242-A Evaporator, report a technetium-99 partition factor of 0.00001 between condensate and residue. Well 299-W15-4, emplaced to monitor groundwater impacts of T-19, yielded abundant evidence for the migration of tritium to groundwater during the active life of the crib; however, at that time, technetium-99 was not an analyte of interest. More recent analyses indicate continuing high tritium values in 299-W15-4, probably indicating that some drainage is still occurring. These later analyses, which include technetium-99, indicate tritium/technetium-99 ratios as high as 12,800, which is probably lower than ratios derived from the evaporator. The most recent data indicate a decreasing ratio, probably indicative of decreasing drainage and/or changing groundwater flow directions.

Figure 3.4 indicates a tritium plume originating at T-19 and extending north and northeast across the 200 West Area. The configuration of this plume indicates that it may be impacting the eastern portions of both WMA TX-TY and WMA T and, in fact, the highest 1997 values for tritium/technetium-99 occur in wells 299-W10-16 and 299-W10-4 (averages of 418 and 156, respectively), located between T and TX-TY. If, as appears likely, this area of higher tritium/technetium-99 ratios (Figure 3.7) is a result of contamination from T-19, then it is a relic of an earlier flow regime with a more northward-flow direction. It would take on the order of 8 years for groundwater to reach 299-W10-16 from T-19, and any present contamination from T-19 will be transported to the northeast, away from the WMAs.

3.2.3 Key Assessment Wells

This section describes chemical variation in the three wells (299-W10-15, 299-W10-17, and 299-W14-12) that initially triggered assessment (trigger wells) at the two WMAs and the chemical variation in well 299-W11-27, which kept WMA T in assessment.

3.2.3.1 WMA T

Well 299-W10-15. Groundwater chemistry in well 299-W10-15, downgradient to WMA-T, has, with the exception of one sampling event in July 1994, changed very little since 1993. High specific conductance in this well (Figure 2.2) principally is a result of elevated sodium and nitrate as indicated in Table 3.1. Specific conductance has declined slowly so that it currently is below the critical mean for the site; however, sodium and nitrate remain high, with nitrate presently exceeding the drinking water standards (Figure 3.8).

-

-

Figure 3.7. Map of Tritium/Technetium-99 in Vicinity of WMAs T and TX-TY

Table 3.1. Average Milliequivalents (meq/L) in Groundwater in Trigger Wells

	W10-15 ^(a,b)	W11-27 ^(c)	W11-27 ^(d)	W10-17 ^(e)	W14-12 ^(f)	W14-12 ^(g)
Sodium	7.24	0.87	1.27	4.89	1.06	1.17
Potassium	0.12	0.11	0.18	0.09	0.18	0.17
Calcium	2.14	2.11	7.52	1.13	8.40	3.71
Magnesium	1.31	1.19	4.16	0.71	4.95	2.18
Alkalinity ^(h)	2.97	2.36	1.92	2.67	NA ⁽ⁱ⁾	1.85
Chloride	0.84	0.06	1.05	1.01	2.68	1.19
Sulfate	1.38	1.19	6.32	1.39	1.84	0.81
Nitrate	5.46	0.09	3.19	2.06	7.74	3.38
Sum	21.46	7.98	25.61	13.95	28.85 ^(j)	14.46
(a) February 1990 through May 1997. (b) All well numbers prefixed by 299-. (c) March 1993 through November 1995. (d) August 1996 through May 1997. (e) May 1991 through May 1997. (f) April 1992 through September 1993. (g) February 1996 through May 1997. (h) At ambient pH essentially all carbonate will be in the form of bicarbonate ion. (i) Not analyzed. (j) Assuming alkalinity = 2.0.						

Other contaminants present above their respective drinking water standards are tritium, gross beta, and fluoride. Technetium-99 is present, but with one exception (July 1994), it has not exceeded the drinking water standard. Comparisons with concentrations in upgradient well 299-W10-16 indicate that well 299-W10-15 has higher concentrations of sodium, nitrate, fluoride, and chromium, and similar concentrations of calcium, sulfate, technetium-99, and tritium. The sodium/calcium ratio has remained fairly constant in both 299-W10-15 (4 to 5 range) and upgradient well 299-W10-16 (3 to 5 range), indicating that both have remained well within the high sodium/calcium-plume. The tritium/technetium-99 ratio in upgradient well 299-W10-16 has remained high (300 to 500 range), indicating it has remained well within the high tritium/ technetium-99 plume; however, this ratio has decreased in well 299-W10-15 from values near 160 to values near 90, indicating that the high tritium/technetium-99 plume is migrating away from this well.

The chemistry of the sample from July 1994 is very similar to that of 299-W11-27 after 1995 and of 299-W14-12 at WMA TX-TY. The analysis is internally consistent with good charge balance and total dissolved solids (TDS) is consistent with the specific conductance measured in the field. Thus, we are left with the possibilities of either a brief period when well 299-W10-15 intercepted a contaminant plume or that an entirely different well was sampled by mistake.

-

-

Figure 3.8. Concentrations (Activities) of Constituents in Wells 299-W10-15 and 299-W10-16

Well 299-W11-27. Groundwater chemistry in well 299-W11-27, a downgradient well at WMA-T, has exhibited a pattern quite distinct from that in 299-W10-15. This well was completed in November 1991, and when groundwater sampling was initiated in May 1992 the concentrations of groundwater constituents were observed to be dropping sharply (Figure 3.9), with specific conductance dropping from approximately 700 to approximately 400 $\mu\text{S}/\text{cm}$ between May 1992 and March 1993 (Figure 2.2). Following the early declines, concentrations remained relatively constant until 1995. In late 1995 and early 1996, groundwater constituents, particularly technetium-99, tritium, nitrate, chromium, calcium, magnesium, sulfate, and total organic carbon (TOC) started a very rapid increase. During this rapid increase, which may have peaked in late 1996 or early 1997, measured values for specific conductivity reached 1,307 $\mu\text{S}/\text{cm}$, technetium-99 reached 21,700 pCi/L, nitrate reached 229,000 ppb, and sulfate reached 326,000 ppb. Examination of Table 3.1 indicates that between 1993 and 1995 principal constituents contributing to specific conductance were calcium and bicarbonate. After 1995, the principal constituents contributing to specific conductance were calcium, magnesium, sulfate, and nitrate.

Concentration and activity plots for well 299-W11-27 and upgradient well 299-W10-16 (Figure 3.9) indicate very distinct differences. Well 299-W11-27 is distinctly higher in technetium-99, calcium, magnesium, sulfate, chromium, and TOC (not shown). Upgradient well 299-W10-16 is higher in sodium, nitrate, and tritium. The drinking water standards for technetium-99, tritium, nitrate, and chromium are exceeded in this well. Cobalt-60 is also present as a co-contaminant but does not exceed its drinking water standard.

The value of sodium/calcium during the period of low specific conductance (1993-1995) averaged 0.46; however, in 1997, it reached values as low as 0.17. This decrease in sodium/calcium, coupled with increasing technetium-99 and its co-contaminants is consistent with a small-volume contaminant source that is strongly affected by ionic exchange in the vadose zone and is quite distinct from values in other network wells. The values for tritium/technetium-99 were near 20 before 1996; however, they have subsequently dropped as low as 0.2. These low values are similar to values observed at WMA S, SX (Johnson and Chou 1997), and are consistent with a tank source of contamination.

Both the increase in technetium-99 and its co-contaminants in well 299-W11-27 and the inflection in water table decline rates occurred in 1995. This correspondence raised the possibility that the contaminants are concentrated in the upper portion of the aquifer and that the observed increases are the result of the declining water table. This would be the case if contaminants reaching the water table were dilute enough, or in small enough volume, that extensive vertical mixing does not occur. To test this hypothesis, a Kabis discrete sampling system was used to sample the top 15 cm (6 in.) of the aquifer for comparison with the pumped sample collected at a depth of approximately 1 m (3 ft) below the water table. The sampling results indicate the opposite, however, and both technetium and specific conductance decrease toward the top of the aquifer. Results for the Kabis sampling and the routine pump sampling are presented in Table 3.2. The technetium result for the pumped sample is approximately 20% higher than that for the Kabis sample, and the actual difference may be somewhat larger because of vertical mixing in the well during pumping. If this result can be confirmed, it may indicate that, contrary to the initial hypotheses, the observed 1997 decline in technetium-99 and other components may be a result of the declining water table.

3.2.3.2 WMA TX-TY

Well 299-W10-17. Specific conductance in well 299-W10-17, a downgradient well at WMA-TX-TY,

has shown little change in specific conductance since the inception of assessment monitoring in 1993,

-

-

Figure 3.9. Concentrations (Activities) of Constituents in Wells 299-W11-27 and 299-W10-16

Table 3.2. Vertical Sampling Results from Well 299-W11-27

Constituent	Kabis Sample ^(a)	Pump Sample ^(b)
Technetium-99 (pCi/L)	13,500	16,000
Tritium (pCi/L)	10,100	9,630
Specific Conductance ($\mu\text{S}/\text{cm}$)	1,067	1,130
(a) Sampler inlet 15 cm (6 in.) below water table.		
(b) Pump inlet approximately 1 m (3 ft) below water table.		

remaining above the critical mean of 668 $\mu\text{S}/\text{cm}$ for the site (Figure 2.2). Average concentrations (meq/L) for ionic species, presented in Table 3.1, indicate that sodium, nitrate, and bicarbonate are the principal constituents responsible for the high specific conductance in this well.

During most of the monitoring history of this well, the chemistry, with the exception of a moderate decrease in nitrate and tritium, has been relatively constant (Figure 3.10). In 1995, however, the decrease in nitrate and tritium reversed and calcium, magnesium, and technetium-99 started to increase. The increase has been modest, with technetium-99 exhibiting a high degree of variability. Examination of Figure 3.10 indicates that well 299-W10-17 has distinctly higher concentrations of sodium, sulfate, and fluoride than upgradient well 299-W15-22. Calcium is distinctly higher in upgradient well 299-15-22. Tritium, nitrate, technetium-99, and chromium are broadly similar in the two wells, although tritium and nitrate are quite variable. Nitrate, tritium, and gross beta exceed drinking water standards in this well.

The values for sodium/calcium in this well are high; however, they have declined from 5.6 in 1991 to 2.5 in 1997. During the same time period, values for tritium/technetium-99 have declined from nearly 400 to approximately 90, with most of the decline occurring after 1995. Apparently, the high sodium/calcium plume and high tritium/technetium-99 are moving toward the northeast, and their effects on this well are decreasing.

Well 299-W14-12. Specific conductance in this well has decreased by approximately 50 percent since 1992 (Figure 2.2); however, it still exceeds the critical mean for WMA TX-TY. As can be seen in Table 3.1, the principal cause for elevated specific conductance continues to be calcium, magnesium, and nitrate, despite a considerable decrease in ionic strength.

The groundwater chemistry in well 299-W14-12 is quite different from that found at well 299-W10-17, a relationship highly analogous to that between wells 299-W10-15 and 299-W11-27 at WMA T. Unlike the case at WMA T, however, contaminant concentrations for well 299-W14-12 were near their highest values when monitoring was initiated (Figure 3.11). In September 1993, contaminant values apparently peaked and have declined from that date until 1996 when they seem to have, at least temporarily, stabilized. As in 299-W11-27, there is a strong correlation between calcium and technetium; however, in this case, they decrease together. Examination of the plots in Figure 3.11 indicates an apparent convergence of concentrations in well 299-W14-12 with those in upgradient well 299-W15-22.

-

-

Figure 3.10. Time-Concentration (Activity) Plots for Groundwater in Wells 299-W10-17 and 299-W15-22

-

-

Figure 3.11. Time-Concentration (Activity) Plots for Groundwater in Wells 299-W14-12 and 299-W15-22

The major contaminants in this well are technetium-99, nitrate, tritium, iodine-129, and cobalt-60. There is a very high degree of correlation between technetium-99 activities and specific conductance and between these two parameters and the other co-contaminants (Figure 3.12). This high degree of correlation is indicative of a coherent source for all of the contaminants. All these co-contaminants, with the exception of cobalt-60, have exceeded or do exceed the drinking water standards.

Values for sodium/calcium were on the order of 0.15 when monitoring first started and since have risen to approximately 0.4. These low initial ratios are consistent with a small-volume, high-sodium contaminant source that exchanged most of its sodium for calcium resulting in a low sodium/calcium ratio. Unlike 299-W11-27, where tritium/technetium-99 values have dropped as low as 0.2, tritium/technetium-99 values for 299-W14-12 range from 24 to 172. In both cases, however, higher technetium-99 activities correlate with lower tritium/technetium-99 values. The higher values for tritium/technetium-99 at 299-W14-12 may be a result of their source; however, it is more probable that the groundwater into which the contaminants are mixing has a larger contribution from T-19.

Another strong, but unexpected, correlation exists between contaminant concentrations and the decline in the water table (Figure 3.13). The correlation between rate of water table decline and rate of contaminant decrease strongly suggests that the decline in contaminant levels is an artifact of water-level decline. A downward increase in contaminants within the aquifer would result in sampling increasingly cleaner groundwater as the aquifer drops past the sampling pump. The increase in tritium/technetium-99 may indicate that the upper portion of the aquifer is more strongly influenced by the plume from T-19.

3.2.4 Compositional Relationships

This section follows up on the discussion of regional patterns presented in Section 3.2.1 and discusses the compositional relationships between three key waste components in the trigger wells at WMA T and WMA TX-TY. These three components; tritium, nitrate, and technetium-99 are not generally affected by solubility or sorption and tend to move together through the vadose zone and groundwater. In addition, the tank waste compositions used for comparison are bulk compositions from Agnew (1997). The most important compositions for the following discussion are those of the tank supernates, which are not yet available for many tanks. In the absence of actual data on the compositions of the aqueous mobile phase within tanks the bulk compositions will give the most accurate estimate for highly soluble components such as tritium, nitrate, and technetium-99. In the following discussion the decay of tritium is ignored; however, it should be noted that approximately 0.5 half-life for tritium has elapsed between 1992 and 1997.

3.2.4.1 Sodium/Calcium

WMA T. In terms of sodium and calcium concentrations, the wells form two distinct groups (Figure 3.14). Downgradient well 299-W11-27 is characterized by low sodium and highly variable calcium. In this well, the cluster of samples with calcium concentrations near 40,000 ppb represents pre-1995 compositions. The higher calcium concentrations represent values since 1995, with technetium-99 increasing rapidly with calcium. The other two downgradient wells and upgradient well 299-W10-16 form a relatively distinct compositional group with sodium greater than 100,000 ppb and calcium less than 60,000 ppb.

Sodium/calcium values for monitoring wells at WMA T are presented in Figure 3.15. Three wells,

including upgradient well 299-W10-16, exhibit a similar range of sodium/calcium values and define

-

-

Figure 3.12. Plots of Technetium-99 versus (a) Tritium, (b) Nitrate, (c) Iodine-129, and (d) Cobalt in Well 299-W14-12

-

-

Figure 3.13. Plots of Specific Conductance, Technetium-99, and Water Table Elevation as Function of Sample or Measurement Date in Well 299-W14-12

-

-

Figure 3.14. Calcium versus Sodium for Monitoring Wells at WMA T. The arrow indicates direction of increasing technetium-99. Well 299-W10-16 is upgradient.

-

-

Figure 3.15. Sodium/Calcium versus Calcium for Monitoring Wells at WMA T. Well 299-W10-16 is upgradient.

subparallel trend lines that indicate mixing of a high sodium/calcium groundwater with a lower sodium/calcium water. Downgradient well 299-W11-27, however, is characterized by a much lower range of values, from approximately 0.5 to as low as 0.13, with the higher values representative of groundwater before the increase in specific conductance and technetium-99 in late 1995. This forms a trend line distinct from the other three wells and indicates the mixing of a low sodium/calcium water with a still lower sodium/calcium water; probably similar to that described for well 299-W10-1.

The behavior of sodium and calcium in wells 299-W10-15, 299-W10-16 (upgradient), and 299-W11-28 is consistent with the principal influence being a large volume source of high-sodium waste (high sodium/calcium). The behavior of sodium and calcium in well 299-W11-27 is consistent with expectations for a low-volume source of high-sodium waste (low sodium/calcium), either within the tank farms or from a crib or trench that received a relatively small effluent volume.

WMA TX-TY. The behavior of sodium and calcium in the wells at WMA TX-TY shows significant differences from well to well (Figure 3.16). Downgradient well 299-W14-12 is characterized by low sodium and highly variable calcium. In this well, both calcium and technetium-99 are decreasing, however, the compositional relationship between the two constituents is very similar to that observed in well 299-W11-27 at WMA T. Sodium and calcium concentrations in downgradient well 299-W10-17 are similar to those observed in the high sodium, high sodium/calcium groundwaters at WMA T (e.g., 299-W10-15). Downgradient well 299-W10-18 and upgradient well 299-W15-22 both exhibit relatively low concentrations of both sodium and calcium and appear to be intermediate between wells 299-W10-17 and 299-W14-12.

Sodium/calcium values for monitoring wells at WMA TX-TY are presented in Figure 3.17. Three wells, including upgradient well 299-W15-22, have relatively low values for sodium/calcium, with 299-W14-12 having the lowest ratios and the highest calcium concentrations. Downgradient well 299-W10-17, however, has calcium concentrations and sodium/calcium values similar to those observed at WMA T, exclusive of well 299-W11-27. The range of sodium/calcium values observed in well 299-W10-17 is somewhat larger than in wells at WMA T and is decreasing.

The behavior of sodium and calcium in well 299-W10-17 is consistent with contamination by a large-volume, high-sodium source (high sodium/calcium). The behavior of sodium and calcium in well 299-W14-12 is consistent with a small-volume, high-sodium contaminant source (low sodium/calcium). The behavior of sodium and calcium in wells 299-W10-18 and 299-W15-22 indicates little influence from either source on upgradient well 299-W15-22, and a small influence from the high sodium/calcium source on downgradient well 299-W10-18.

3.2.4.2 Tritium/Technetium-99

Tritium and technetium are fission products that occur in tank waste at WMA T and WMA TX-TY at roughly equal activities. Tritium and technetium-99 concentrations in tank waste indicate average tritium/technetium values of 0.7 for the T Tank Farm and 1.5 for the TX Tank Farm (Agnew 1997).

-

-

Figure 3.16. Calcium versus Sodium for Monitoring Wells at WMA TX-TY. The arrow indicates direction of increasing technetium-99. Well 299-W15-22 is upgradient.

-

-

Figure 3.17. Sodium/Calcium versus Calcium for Monitoring Wells at WMA TX-TY. Well 299-W15-22 is upgradient.

WMA T. Tritium/technetium-99 ratios for wells at WMA T define two groupings, identical to the groupings defined by the sodium/calcium ratios. This grouping is evident in Figure 3.18, a plot of tritium/technetium-99 against technetium-99.

Values for wells 299-W10-15, 299-W10-16 (upgradient), and 299-W11-28 define a mixing line between high-tritium, low-technetium-99 component and a high-tritium, high-technetium (low ratio) component. The high-tritium, low-technetium component probably represents evaporator condensate discharged to the T-19 Crib and Tile Field, and the other component probably represents past practice disposal of tank supernate to various cribs, trenches, and tile fields.

Values for well 299-W11-27 seem to define two trends, one for 1992 through mid-1995 and the other for late 1995 to the present. The earlier trend is essentially parallel to that of the other wells in the network, but is offset toward lower ratios and lower technetium-99 activities. This offset is consistent with the observed chemistry for this well and indicates dilution or mixing with a low tritium/technetium-99, low technetium-99 water. The post-1995 trend is toward higher technetium-99 activities and directly toward reported tank waste activities and ratios. It seems likely that the dilution effect observed from 1992 through mid-1995 was a result of surface water influx and a probable source is discussed in Section 4.1.2. Surface water discharge in the 200 West Area ceased in mid-1995, however, some vadose drainage probably has continued and some dilution effect is still present. This continued dilution would affect the top portion of the aquifer and may well explain the observed decrease in contaminant concentrations at the top of the aquifer. This continued dilution would also affected how closely the groundwater composition approached that of the tank source.

WMA TX-TY. Tritium/technetium-99 versus technetium-99 plots for wells at WMA TX-TY are presented in Figure 3.19. Three of the wells; 299-W10-17, 299-W10-18, and 299-W15-22 (upgradient) define a mixing line similar to that of the three well grouping at WMA T, indicating mixing of similar components. Well 299-W14-12 defines a mixing line that extends from the three well line toward the tank compositions, indicating mixing of tank waste compositions with water similar to that observed in other network wells. The approximately four orders of magnitude between the maximum reported values of technetium-99 in groundwater and reported tank activities indicates that a very small tank contribution can have a significant effect on groundwater.

3.2.4.3 Nitrate/Technetium-99

Nitrate and technetium-99 are significant components of tank waste, both exist in groundwater as highly insoluble anions, and they tend to migrate together. Nitrate, however, may also be contributed by discharges of nitric acid to cribs at the PFP and in this case would not be accompanied by high tritium or technetium-99. Thus, examination of the nitrate/technetium-99 ratio offers the possibility of identifying this alternative source of groundwater nitrate.

WMA T. Nitrate/technetium-99 ratios for wells at WMA T define two groupings, identical to the groupings defined by the sodium/calcium and tritium/technetium ratios. This grouping is evident in Figure 3.20, a plot of nitrate/technetium-99 against technetium-99.

Values for wells 299-W10-15, 299-W10-16 (upgradient), and 299-W11-28 define a mixing line between high-nitrate, low-technetium-99 (high ratio) component and a high-tritium, high-technetium (low

ratio) component. The high-nitrate, low-technetium component probably represents the influence of PFP discharges on

-

-

Figure 3.18. Plot of Tritium/Technetium-99 versus Technetium-99 for Wells at WMA T.
Well 299-W10-16-22 is the upgradient well. Tank data from Agnew (1997).

-

-

Figure 3.19. Plot of Tritium/Technetium-99 versus Technetium-99 for Wells at WMA TX-TY.
Well 299-W15-22 is the upgradient well. Tank data from Agnew (1997).

groundwater compositions, and the other component probably represents past practice disposal of tank supernate to various cribs, trenches, and tile fields. The pattern of nitrate and technetium in well 299-W11-27 is essentially identical to that of tritium and technetium-99 and a similar explanation is reasonable.

WMA TX-TY. A plot of nitrate/technetium-99 versus technetium-99 for wells at WMA TX-TY (Figure 3.21) shows all four well network wells defining similar mixing lines between a high-nitrate, low-technetium component (PFP) and a high-nitrate, high-technetium-99 (low ratio), tank waste like, component. The principal difference between well 299-W14-12 and the other wells is that its compositions extends further down the mixing line toward the tank waste composition.

3.3 Depth Variability

Variation of contaminant concentrations with depth is significant because of its impact on determinations of quantity and extent of contamination and because of information that it may provide about vadose transport mechanisms. Within the groundwater system beneath the WMAs there are two potential causes of contaminant stratification within the aquifer. The first is for brines (“high-salt waste”), with densities significantly greater than 1 g/cm^3 , to sink within the aquifer. The second potential cause of stratification within the aquifer is recharge with little, or incomplete, vertical mixing; resulting in layering at the top of the aquifer.

By sampling with a pump set at a fixed depth there is the possibility, in a vertically inhomogeneous aquifer, that we are not sampling the highest contaminant concentrations or are missing the contaminants completely. There is little available data on vertical distribution of contaminants in the vicinity of WMAs T and TX-TY; however, available data indicates that it may be an important factor. Preliminary vertical sampling results at well 299-W11-27 at WMA T indicate a vertical gradient for technetium-99 and other constituents in the upper portion of the aquifer. Sampling of the top 30 cm (1 ft) of the aquifer using a Kabis sampler indicates a decrease of approximately 20% from technetium-99 activities reported from the pumped sample from a depth of approximately 1 m (3 ft). Given that some vertical mixing occurred during pumping, the actual difference is probably somewhat larger. Thus, the decline in contaminant concentrations observed in 1997 may be a result of declining water levels, and not of actual contaminant concentrations. In addition, the evidence for a high degree of correlation between contaminant concentration decline and water level decline in WMA TX-TY well 299-W14-12 (Figure 3.13) offers strong circumstantial evidence for a vertical contaminant gradient within the upper portion of the aquifer. A schematic illustration of how sample contaminant concentration may be affected by vertical stratification in a declining aquifer is presented in Figure 3.22.

The evidence for vertical gradients within the aquifer is significant for understanding vadose transport mechanisms because of the possibility of both density driven transport and surface infiltration driven transport (Ward et al. 1997). The observed variations in wells 299-W11-27 and 299-W14-12 may indicate that the observed peaking out of contaminant concentrations are a result of declining water levels and not of declining contaminant concentrations within the aquifer. It may also indicate that contamination is more extensive than indicated by sampling of the upper portion of the aquifer.

-

-

Figure 3.20. Plot of Nitrate/Technetium-99 versus Technetium-99 for Wells at WMA T.
Well 299-W10-16-22 is the upgradient well. Tank data from Agnew (1997).

-

-

Figure 3.21. Plot of Nitrate/Technetium-99 versus Technetium-99 for Wells at WMA TX-TY.
Well 299-W15-22 is the upgradient well. Tank data from Agnew (1997).

-

Figure 3.22. Schematic Illustration of Decrease in Observed Contaminant Concentrations as a Stratified Aquifer Drops Past the Pump Inlet

3.4 Evidence of Driving Forces

The major driving forces for pushing contaminants through the vadose zone at WMAs T and TX-TY, other than their own volumes and densities, appear to be surface infiltration through the gravels that cover both WMAs and surface run-off, principally from rapid snow melt.

The high infiltration rate through course-grained, unvegetated covers has been amply discussed by Gee (1987), Gee et al. (1992), and Fayer and Walters (1995). In addition, both WMAs are located at the bottom of a natural depression that will tend to catch any ponded surface runoff. This is particularly a problem at WMA T, where slopes immediately adjacent to the WMA, particularly along the east side, tend to funnel surface runoff directly into the tank farm. The reality of this problem is amply illustrated by the photos (Figure 3.23) of the T Tank Farm taken after a rapid snow melt event in February 1979. There is little doubt that the water ponded over and around the tanks infiltrated the vadose zone and acted as a driving force for any existing vadose zone contamination. There is also little doubt that this is not the only event of this type that has occurred.

-

-

Figure 3.23. Photos Showing Flooding of the T Tank Farm after a Rapid Snow Melt Event in February 1979. Area shown is around Tank T-106.

4.0 Conceptual Model

This section evaluates three possibilities for explaining the contaminants observed in downgradient wells at WMA T and WMA TX-TY to determine whether an upgradient source can account for the observed groundwater contamination. The possibilities are:

1. interception of large-scale contaminant plumes resulting from past-practice discharges to the soil column
2. interception of a smaller scale contaminant plume from one of the cribs or ditches adjacent to the WMAs
3. interception of a contaminant plume resulting from tank leak or spill materials from within the tank farms.

4.1 WMA T

The T Tank Farm (WMA T) is particularly interesting from a groundwater contamination point of view. Among the seven confirmed or suspected leakers in this tank farm, T-106 had the largest documented tank leak volume, an estimated 435,000 L (115,000 gal) (Routson et al. 1979). In addition, a less well-documented spill at T-101, apparently resulting from overfilling the tank, may have resulted in a release volume well in excess of the volume of the T-106 leak (Routson 1981). Routson (1981) reported cesium-137 activities of 2 $\mu\text{Ci/g}$ at a depth of more than 37 m (122 ft) in well 50-01-04, adjacent to the T-101 tank.

In WMA T, only one well (299-W10-15) triggered the site into assessment; however, subsequently a second well (299-W11-27) exceeded both the critical mean for specific conductance and the drinking water standards for several constituents. Both wells need to be considered in deciding whether to proceed with assessment monitoring and evaluation.

4.1.1 Well 299-W10-15

This well is located at the northwest corner of WMA T and, given a northeast groundwater flow direction, currently is not downgradient to the WMA (Figure 2.1). Examination of contour maps of sodium/calcium (Figure 3.5) and specific conductance (Figure 3.6) and the discussion regarding those relationships indicate that the principal influence on 299-W10-15 is the sodium-nitrate-tritium plume that extends from west and south of WMA-T across WMA-T and the northern portion of WMA TX-TY. Thus, it is concluded that the high specific conductance, nitrate, and tritium in this well are a result of past-practice waste disposal activities and do not have a present day tank farm source.

4.1.2 Well 299-W11-27

This well, located at the northeast corner of the WMA, is clearly downgradient to the T Tank Farm

(Figure 2.1). The groundwater chemistry sampled by this well has been highly variable, changing relatively rapidly between concentration values both above and below values that might be expected for this area (Figure 3.9).

The rapid concentration decline for all groundwater constituents during 1992-1993, with specific conductances dropping to values near 400 $\mu\text{S}/\text{cm}$ (Figure 2.2), may be explained by the close proximity of the well to a 61 cm (24 in.) vitrified clay pipe. This pipe carried water from the 207-T Retention Basin to the T-4-2 Ditch. Cable tool drilling of 299-W11-27, immediately adjacent to the pipe, may have seriously damaged the pipe and resulted in a water source in close proximity to the well. Movement of effluent water to the water table adjacent to the well would explain the low concentrations and relatively low specific conductances observed from 1993-1995.

If leakage from a waste water line adjacent to 299-W11-27 is the cause of the low specific conductance water observed before 1995, then the sudden appearance of contaminants can easily be explained. In this model, contaminants were present in groundwater before 1995, but were diluted or diverted away from 299-W11-27 by water entering from above. If sufficient water leaked, there may even have been a slight groundwater mound in the vicinity of the well. Elimination of water discharge to the T-4-2 Ditch, via the broken pipeline, in 1995 allowed normal groundwater flow directions to resume and the contaminants to reach the well.

There appears to be no obvious source for the contaminants upgradient to the WMA. The areas to the west and south of the WMA, where adjacent cribs have impacted groundwater, are dominated by high sodium, high sodium/calcium, high tritium/technetium-99, and relatively low technetium-99 groundwater compositions, completely unlike the contaminant pattern observed in 299-W11-27. In addition, wells 29-W10-8 and 299-W11-23, which bracket 299-W11-27, and are separated by only 55 m (180 ft), are not affected by the plume. This lack of lateral spreading (dispersion) is suggestive of a nearby source.

The preponderance of evidence, as discussed above, indicates a contaminant source within the WMA. The most obvious possibility is T-101, both because of its proximity to the northeast corner of the tank farm and because of the potential size of the reported spill. Currently, however, T-106, or some other as yet unidentified source within the tank farm, cannot be ruled out.

The fact that the plume detected in well 299-W11-27 has gone undetected in wells on both sides of 299-W11-27 (299-W10-8 and 299-W11-24) raises serious questions about the adequacy of monitoring networks around the tank farm WMAs. Wells 299-W10-8 and 299-W11-24 are separated by approximately 55 m (180 ft), far less than the average spacing of RCRA wells around the tank farm WMAs.

4.2 WMA TX-TY

WMA TX-TY lacks the large reported leaks and spills of WMA T; however, five of the six tanks in the TY Tank Farm are suspected leakers, and eight of 18 tanks in the TX Tank Farm are suspected leakers. In addition, although at least twice the size of WMA T, WMA TX-TY still has only the RCRA minimum of one upgradient and three downgradient wells.

WMA TX-TY was triggered into assessment because specific conductance in two downgradient wells, 299-W10-17 along the northern boundary of the WMA, and 299-W14-12 east of the WMA, exceeded the critical mean for the facility. The relationship between the chemistry of these two wells is similar to that

between wells 299-W10-15 and 299-W11-27 at WMA T; however, in this case, unlike well 299-W11-27 at WMA T, groundwater sampled by well 299-W14-12 had elevated technetium-99 and its co-contaminants from the initiation of sampling.

4.2.1 Well 299-W10-17

Well 299-W10-17, located along the northern boundary of WMA TX-TY (Figure 2.1), is marginally downgradient to the WMA with current groundwater flow direction. Like well 299-W10-15 at WMA T, the principal influences on the chemistry of groundwater in this well are the plume of high sodium/calcium, high specific-conductance groundwater that extends eastward across WMA T and the northern portion of WMA TX-TY (Figures 3.5 and 3.6), and the high tritium/technetium-99 plume extending northward from T-19. Thus, the high sodium and nitrate that are the cause of the high specific conductance and the high tritium are a result of older waste disposal practices outside of the WMA and not a result of tank farm contaminants reaching groundwater.

4.2.2 Well 299-W14-12

In terms of temporal variation, compositional variation in well 299-W14-12 is the inverse of that observed in well 299-W11-27 at WMA T. In terms of contaminant chemistry, however, they are very similar. The overall contaminant pattern, including high technetium-99, high nitrate, high calcium, high magnesium, and low sodium are consistent with a small-volume, high-sodium contaminant source.

Because the contamination was present at near its maximum concentration when well 299-W14-12 was drilled, it is impossible to place a duration on the plume passing this well. In addition, it is impossible at this time to determine whether the contaminant levels in this well are decreasing because changing groundwater flow directions are moving the plume away from the well, or because of higher contaminant concentrations deeper in the aquifer (i.e., the contaminant zone may be dropping below the fixed pump intake as the water level declines).

Given current groundwater flow direction, there are two potential sources for the contaminants observed in 299-W14-12, the TX Tank Farm within WMA TX-TY or the series of specific retention trenches located west of the WMA (Figure 2.1). Trenches T-21, 22, 23, and 24, active in 1954, received volumes of tank supernate ranging from 0.46 to 1.53 million liters. Trench T-25, also active in 1954, received 3 million liters of evaporator bottoms from the 242-T Evaporator and is the only trench in this group that may have significantly exceeded the underlying vadose zone pore volume. The lack of monitoring wells between these trenches, particularly the T-25 Trench, and the WMA makes consideration of their role in the observed contamination at well 299-W14-12 a moot point for the purposes of Phase I assessment. Without direct evidence of an upgradient source it cannot be considered. Determination of the effects, if any, of these trenches will, however, have priority in the Phase II assessment work for this WMA.

Given that the chemistry of the contamination observed in well 299-W14-12 is consistent with a source within the WMA, and that there is no direct evidence for a source upgradient to the WMA, it must be concluded that WMA TX-TY has and may still be contaminating groundwater.

5.0 Conclusions

Available evidence indicates, with a high degree of certainty, that WMA T is the source of groundwater contamination in downgradient monitoring well 299-W11-27. Both contaminant chemistry, which indicates a small volume, tank waste source, and lack of lateral spreading in groundwater (dispersion) are indicative of a source within the tank farm. Drinking water standards in this well are exceeded for technetium-99, tritium, nitrate, gross beta, and chromium. The largest exceedance is for technetium-99, which is present at activity levels approximately 20 times the drinking water standard of 900 pCi/L.

Available evidence is consistent with a WMA TX-TY source for the groundwater contamination in downgradient monitoring well 299-W14-12. Contaminant chemistry is consistent with a small volume tank waste source. At this time, however, an upgradient source (the T-25 Trench) cannot be completely ruled out. For the purposes of this assessment, given the lack of direct evidence for a source upgradient to the WMA, it must be assumed that WMA TX-TY is the source of groundwater contamination in well 299-W14-12. Because of this uncertainty, Phase II assessment characterization will begin with installation of a new upgradient well to allow evaluation of the potential upgradient source. Contaminant levels in 299-W14-12 have declined to a point where only nitrate and tritium exceed drinking water standards. At peak contaminant levels, technetium-99 was present at concentrations approximately 15 times the drinking water standards and chromium was present at levels approximately 10 times the drinking water standards.

Preliminary evidence from wells 299-W11-27 and 299-W14-12 indicates that contaminant concentrations may increase downward within the aquifer. If the aquifer is stratified with respect to contaminant concentration, it has important implications for the source and transport mechanisms within the vadose zone and about the extent of contamination within the aquifer.

5.1 Recommendations

5.1.1 Compliance Issues

The existing RCRA groundwater monitoring networks are going dry because of a rapidly declining water table. It is important to maintain the minimum legal monitoring requirements and, at the same time, enhance the network to a more defensible level of efficiency. To accomplish this, efforts should be made to deepen the existing well, use older non-RCRA wells where appropriate, and drill new wells where necessary.

5.1.2 Near-Term Corrective Measures

Infiltration of surface water is an important driving force for moving contaminants downward through the vadose zone; therefore any measure that reduces infiltration of surface water has a potential for reducing future groundwater contamination. This includes reducing infiltration from natural causes such as surface runoff and ponding of snow melt, and eliminating man made sources to the extent possible.

5.1.3 Phase II Assessment Objectives

The Phase I assessment conclusions for the two WMAs are different enough to warrant, at least initially, different paths in Phase II assessment.

WMA T. Phase I assessment has been completed without finding credible evidence that sources other than the WMA are responsible for the observed contamination in downgradient well 299-W11-27. Thus, assessment must proceed into Phase II with determination of the extent, concentration, and rate of migration of the contaminants. A Phase II Assessment Plan will be prepared to guide this work and will replace the Phase I Assessment Plan (Caggiano and Chou 1993) as the guiding document. Objectives for Phase II assessment activities to be set forth in this plan are as follows:

- use well-deepening and drilling activities, along with discrete depth sampling in older wells with long perforated intervals, to obtain a three-dimensional picture of groundwater contamination at the two WMAs
- determine the need for additional wells to determine the rate and extent of contaminant migration from the WMAs
- evaluate available data, including spectral gamma surveys of T and TX-TY planned for this year, to identify potential contaminant sources and pathways within the WMAs
- define water-level measurements and evaluations to allow more accurate determination of local groundwater flow directions.

WMA TX-TY. Phase I assessment has been completed without finding credible evidence that sources other than the WMA are responsible for the observed contamination in downgradient well 299-W14-12. Because of changing groundwater flow directions, however, the potential role of upgradient sources (e.g., T-25 Trench) could not be fully evaluated during Phase I. Therefore, the initial step in Phase II evaluation at WMA TX-TY will be the drilling of a new upgradient well between the T-25 Trench and the WMA.

- If no evidence for impact by the T-25 Trench is indicated by groundwater analyses from the new well, Phase II assessment will proceed as outlined for WMA T.
- If evidence from the new upgradient well indicates that the T-25 Trench is the source of observed groundwater contamination in well 299-W14-12, WMA TX-TY will be returned to detection level monitoring.

6.0 References

- Agnew, S. F. 1997. *Hanford Tank Chemical and Radionuclide Inventories: HOW Model Rev. 4*. LA-UR-96-3860, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Alexander, D. J., S. D. Evelo, V. G. Johnson, and M. D. Sweeney. 1995. *Groundwater Impact Assessment Report for the 216-T-4-2 Ditch*. Westinghouse Hanford Company, Richland, Washington.
- Anderson, J. D. 1990. *A History of the 200 Area Tank Farms*. WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Caggiano, J. A., and C. J. Chou. 1993. *Interim-Status Groundwater Quality Assessment Plan for the Single Shell Tank Waste Management Areas T and TX-TY*. WHC-SD-EN-AP-132, Westinghouse Hanford Company, Richland, Washington.
- Caggiano, J. A., and S. M. Goodwin. 1991. *Interim-Status Groundwater Monitoring Plan for the Single-Shell Tanks*. WHC-SD-EN-AP-012, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Colby, S. A., and C. A. Petersen. 1995. *Inventory of Technetium 99 From Reprocessing Hanford Spent Nuclear Fuel*. Letter Report dated April 28, 1995, Correspondence No. 71210-95-013, Westinghouse Hanford Company, Richland, Washington.
- Connelly, M. P., K. A. Lindsay, L. Borghese, and B. H. Ford. 1992. *Hydrogeologic Model for 200 West Groundwater Aggregate Area*. WHC-SD-EN-TI-014, Westinghouse Hanford Company, Richland, Washington.
- Delaney, C. D., K. A. Lindsay, and S. P. Reidel. 1991. *Geology and Hydrology of the Hanford Site: A Standardized Text for use in Westinghouse Hanford Company Documents and Reports*. WHC-SD-ER-TI-003, Westinghouse Hanford Company, Richland, Washington.
- Dresel, P. E., L. C. Swanson, H. Hampt, F. N. Hodges, R. B. Mercer, S. M. Narbutovskih, and B. A. Williams. 1997. *200 West Areas, Chapter 6.9, in Hanford Site Groundwater Monitoring for Fiscal Year 1996*, M. J. Hartman and P. E. Dresel, (eds.). PNNL-11470, Pacific Northwest National Laboratory, Richland, Washington.
- Dresel, P. E., J. T. Rieger, W. D. Webber, P. D. Thorne, B. M. Gillespie, S. P. Luttrell, S. K. Wurstner, T. L. Liikala. 1996. *Hanford Site Groundwater Monitoring for 1995*. PNNL-11141, Pacific Northwest National Laboratory, Richland, Washington.
- Fayer, M. J., and T. B. Walters. 1995. *Estimated Recharge Rates at the Hanford Site*, PNL-10285, Pacific Northwest National Laboratory, Richland, Washington.
- Gee, G. W. 1987. *Recharge at the Hanford Site: Status Report*. PNL-6403, Pacific Northwest National Laboratory, Richland, Washington.

Gee, G. W., M. J. Fayer, M. L. Rockhold, and M. D. Campbell. 1992. "Variations in Recharge at the Hanford Site." *Northwest Sci.*, 66:237-250.

Graham, M. J., M. D. Hall, S. R. Strait, and W. R. Brown. 1981. *Hydrology of the Separations Area*. RHO-ST-42, Rockwell Hanford Operations, Richland, Washington.

Jensen, E. J., S. P. Airhart, M. A. Chamness, T. J. Gilmore, D. R. Newcomer, and K. R. Oster. 1989. *40 CFR 265 Interim-Status Ground-Water Monitoring Plan for the single-Shell Tanks*. WHC-SD-EN-AP-012, REV. 0, Westinghouse Hanford Company, Richland, Washington.

Johnson, V. G. 1993. *Westinghouse Hanford Company Operational Groundwater Status Report*. WHC-EP-0595, Westinghouse Hanford Company, Richland, Washington.

Johnson, V. J. 1997. *Vadose Zone Contamination, Chapter 4.0 in Hanford Site Groundwater Monitoring for Fiscal Year 1996*, M. J. Hartman and P. E. Dresel, (eds.). PNNL-11470, Pacific Northwest National Laboratory, Richland, Washington.

Johnson, V. J., and C. J. Chou. 1998. *Results of Phase I Groundwater Quality Assessment for Single-Shell Tank Waste Management Areas S-SX at the Hanford Site*, Pacific Northwest National Laboratory, PNNL-11810, Richland, Washington.

Lindsay, K. A. 1995. *Miocene- to Pliocene-Aged Suprabasalt Sediments of the Hanford Site, South-Central Washington*. BHI-00184, Bechtel Hanford, Inc., Richland, Washington.

Lindsay, K. A., M. P. Connelly, and B. N. Bjornstad. 1991. *Geologic Setting of the 200 West Area: An Update*. WHC-SD-EN-TI-008, Westinghouse Hanford Company, Richland, Washington.

Price, S. M., R. B. Casper, M. K. Additon, R. M. Smith, and G. V. Last. 1979. *Distribution of Plutonium and Americium Beneath the 216-Z-1A Crib: A Status Report*. RHO-ST-17, Rockwell Hanford Operations, Richland, Washington.

Rohay, V. J. 1994. *1994 Conceptual Model of the Carbon Tetrachloride Contamination in the 200 West Area at the Hanford Site*. WHC-SD-EN-TI-248, Westinghouse Hanford Company, Richland, Washington.

Routson, R. C., W. H. Price, D. J. Brown, and K. R. Fecht. 1979. *High-Level Waste Leakage from the 241-T-106 Tank at Hanford*. RHO-ST-14, Rockwell Hanford Operations, Richland, Washington.

Routson, R. C. 1981. "Volume of Sediments Contaminated with ⁹⁰Sr and ¹³⁷Cs in the T-Tank Farm," letter from R. C. Routson to W. F. Heine, No. 72710-81-120, dated May 25, 1981, WIDS.

Routson, R. C., and V. G. Johnson. 1990. "Recharge Estimates for the Hanford Site 200 Areas Plateau." *Northwest Sci.*, 64:150-158.

Tallman, A. M., K. R. Fecht, M. C. Marratt, and G. V. Last. 1979. *Geology of the Separations Areas, Hanford Site, South-Central Washington*. RHO-ST-23, Rockwell Hanford Operations, Richland,

Washington.

U.S. Department of Energy, Richland Operations Office (DOE/RL). 1992. *T Plant Source Aggregate Area Management Study Report*. DOE/RL-91-61, U.S. Department of Energy, Richland, Washington.

U.S. Department of Energy, Richland Operations Office (DOE/RL). 1993. *200 West Groundwater Aggregate Area Management Study Report*. DOE/RL-92-16, U.S. Department of Energy, Richland, Washington.

Ward, A. L., G. W. Gee, and M. D. White. 1997. *A Comprehensive Analysis of Contaminant Transport in the Vadose Zone Beneath Tank SX-109*, PNNL-11463, Pacific Northwest National Laboratory, Richland, Washington.